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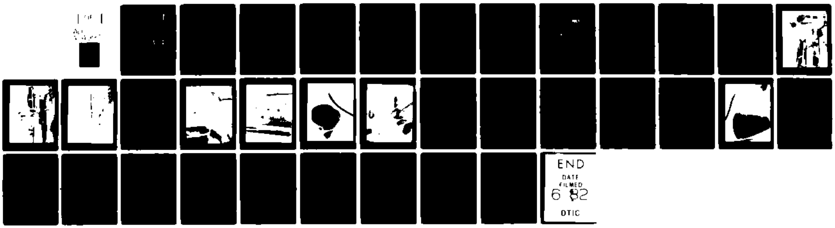

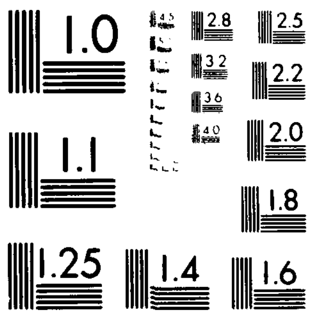

MICROCOPY RESOLUTION TEST CHART

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An Evaluation of Occupational Exposure to Hydrazine (H-70) During Routine Maintenance Tasks Associated with the F-16 Emergency Power Unit

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USAF OEHL TECHNICAL REPORT

AN EVALUATION OF OCCUPATIONAL EXPOSURE TO HYDRAZINE (H-70) DURING ROUTINE MAINTENANCE TASKS ASSOCIATED WITH THE F-16 EMERGENCY POWER UNIT

MARCH 1978

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PREPARED FOR:

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TECHNICAL REPORT NO. 78-23
PROJECT 77-27

AN EVALUATION OF OCCUPATIONAL EXPOSURE TO HYDRAZINE (H-70) DURING ROUTINE MAINTENANCE TASKS ASSOCIATED WITH THE F-16 EMERGENCY POWER UNIT

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ABSTRACT

During the week of 23 to 27 January 1978, a survey team from the USAF Occupational and Environmental Health Laboratory conducted an analysis of maintenance tasks associated with the F-16 Emergency Power Unit (EPU). This analysis involved definition of tasks for both aircraft and hydrazine fill stand activities and included the collection of personal and short period air samples to define airborne exposure to hydrazine during these tasks. The tasks which were identified include: nitrogen depressurization, catalyst purge, poppet valve replacement and the entire refilling procedure. Measurements indicate compliance with a Time Weighted Average value of 0.1 ppm hydrazine, however, potential peak exposures which range as high as 5 to 8 ppm do occur during some tasks. A technician would be unaware of many such exposures since concentrations below the odor threshold of 3 to 5 ppm give no warning but are at least an order of magnitude above acceptable occupational exposure limits. Recommendations are provided for the elimination of these sources of potential peak exposure and for the use of personal protective equipment during specific tasks.

1. Introduction: The F-16 aircraft built by General Dynamics is a single engine air combat fighter which employs a flight control system referred to as "fly by wire." The control surfaces of the aircraft are operated by electrical or hydraulic servomotors, which normally receive power from the aircraft's engine. The aircraft will rapidly become unstable if electrical or hydraulic power is lost. For this reason, it has been necessary to equip the F-16 with a highly reliable and quickly responsive method of developing emergency electrical and hydraulic power. A monopropellant system using an azeotropic mixture of seventy percent hydrazine, thirty percent water (by volume) was selected for this purpose (Figure 1). At the request of the F-16 Systems Project Office (SPO), the USAF Occupational and Environmental Health Laboratory (USAF OEHL) conducted an evaluation of occupational exposures received by aircraft maintenance personnel during routine maintenance of the hydrazine fueled emergency power unit (EPU). Recommendations for engineering modifications, changes to work practices, and personal protective equipment are provided, and are based on observations and measurements made during the survey. The protective equipment recommendations are specific to the maintenance procedures and aircraft configuration at the time of the survey and should be re-evaluated as engineering modifications reduce the release of hydrazine into the occupational environment.

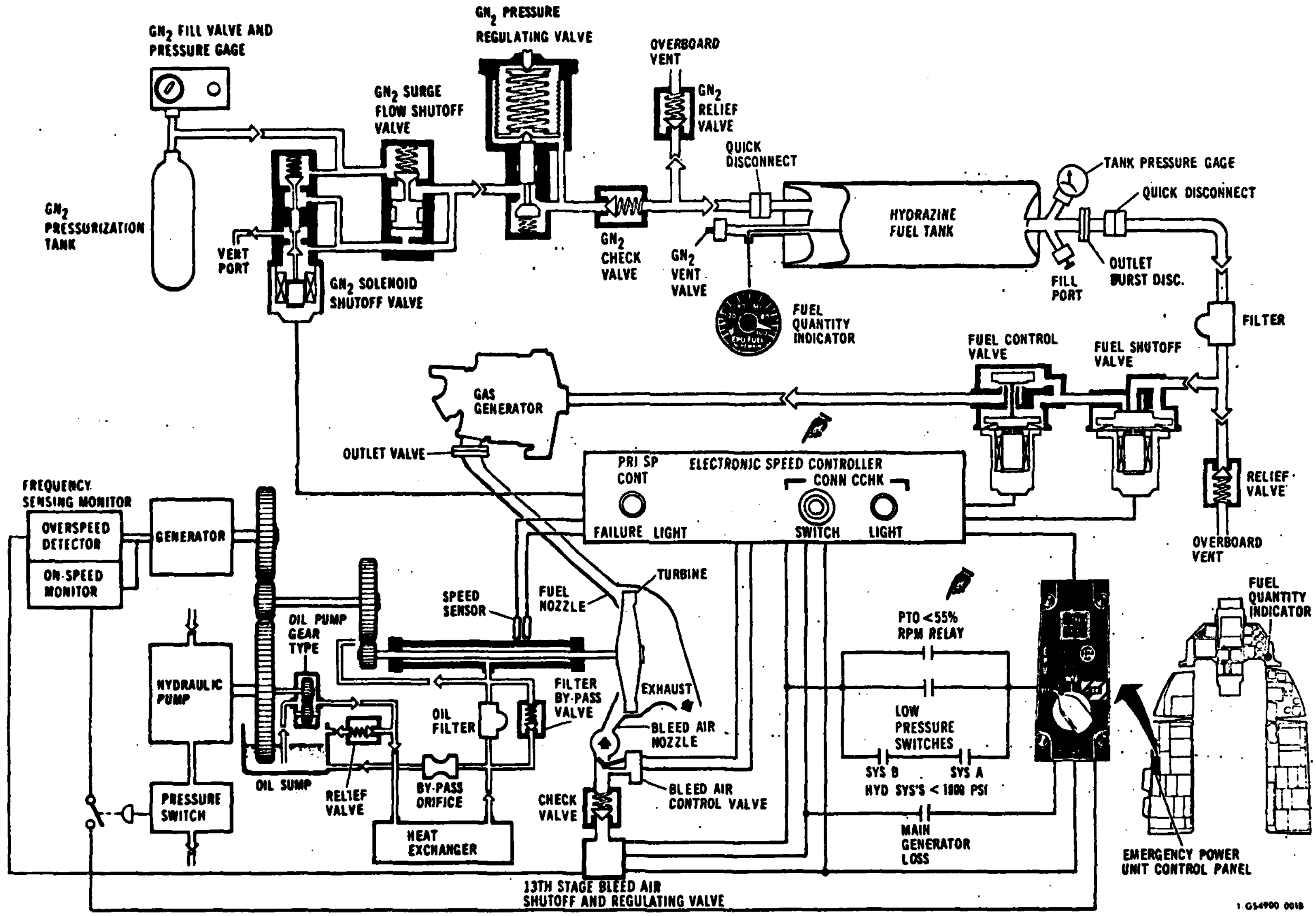


FIGURE 1. EMERGENCY POWER UNIT SCHEMATIC

2. Standard for Occupational Exposure

a. Executive Order 11807, as implemented by The Department of Defense and the USAF, requires that the USAF apply occupational exposure criteria which is equal to, or more restrictive than that mandated under the Occupational Safety and Health Act of 1970. For the purposes of this project, the 70:30 mixture of hydrazine and water (H-70) was treated as being toxicologically identical to "neat" (100%) hydrazine. The recommended Threshold Limit Value (TLV) for hydrazine as established by the American Conference of Governmental Industrial Hygienists Inc. (ACGIH, Inc.), is the criterion which the USAF uses. The 1977-78 TLV for hydrazine is 0.10 parts per million (ppm) at 25°C and 760 mm Hg as a Time Weighted Average (TWA). The TWA concept permits excursions above the limit, provided that such excursions are compensated by exposure below the limit during the workday. Based on presently accepted toxicology of hydrazine, a "rule of thumb" excursion factor of three is considered acceptable. This leads to a permissible excursion of 0.30 ppm.

b. The current TLV-TWA for hydrazine was accepted by the ACGIH Inc. in 1977 and it is listed as an industrial substance suspect of carcinogenic potential for man. Included in their definition are "chemical substances or substances associated with industrial processes, which are suspect of inducing cancer, based on either (1) limited epidemiological evidence, exclusive of clinical reports of single cases, or (2) demonstration of carcinogenesis in one or more animal species by appropriate methods."[2] For hydrazine, this categorization was based on the tumor incidence in mice one year after a chronic 6 month inhalation exposure.

c. While the USAF applies the standard discussed in the preceding two paragraphs, a discussion of standards for exposure would be incomplete without a review of current developments in the Occupational Safety and Health Administration (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) which is the federal agency responsible for advising OSHA on changes to mandatory exposure limits. NIOSH has prepared a draft criteria document on the hydrazines which, when published, will serve as a recommendation to OSHA. The recommended maximum exposure value in the draft document is 0.07 ppm of hydrazine during any fifteen minute period. This recommendation is based on NIOSH's opinion that valid, statistically significant evidence of tumor induction in experimental animals is relevant to human exposure. Their exposure value is based on the lowest reliably detectable concentration using the recommended NIOSH air sampling technique.

d. OSHA has published their intent to promulgate a generic standard for all substances which pose a potential occupational carcinogenic risk. A potential occupational carcinogen is defined as "any toxic substance which (1) causes, at any level of exposure or dose, as a result of any oral, respiratory, or dermal exposure, or any other exposure which results in the systemic distribution of the substance under consideration, in the organism tested, an increased incidence of benign or malignant neoplasms, or a combination thereof, in (i) humans or (ii) one or more experimental mammalian test species, or (2) in a statistically significant manner decreases the latency period between exposure and onset of neoplasms in (i) humans or (ii) in one or more mammalian species." For a substance in this category, the permissible exposure limits will "reflect the lowest feasible levels and, when it is determined by OSHA (sic) that there are suitable substitutes that are less hazardous to humans, no occupational exposure shall be permitted."[18] No exposure is further defined to include a system in which the substance is totally confined, i.e., a closed system. Public hearings on the proposed standard are scheduled to begin in the summer of 1978.

3. Task Description

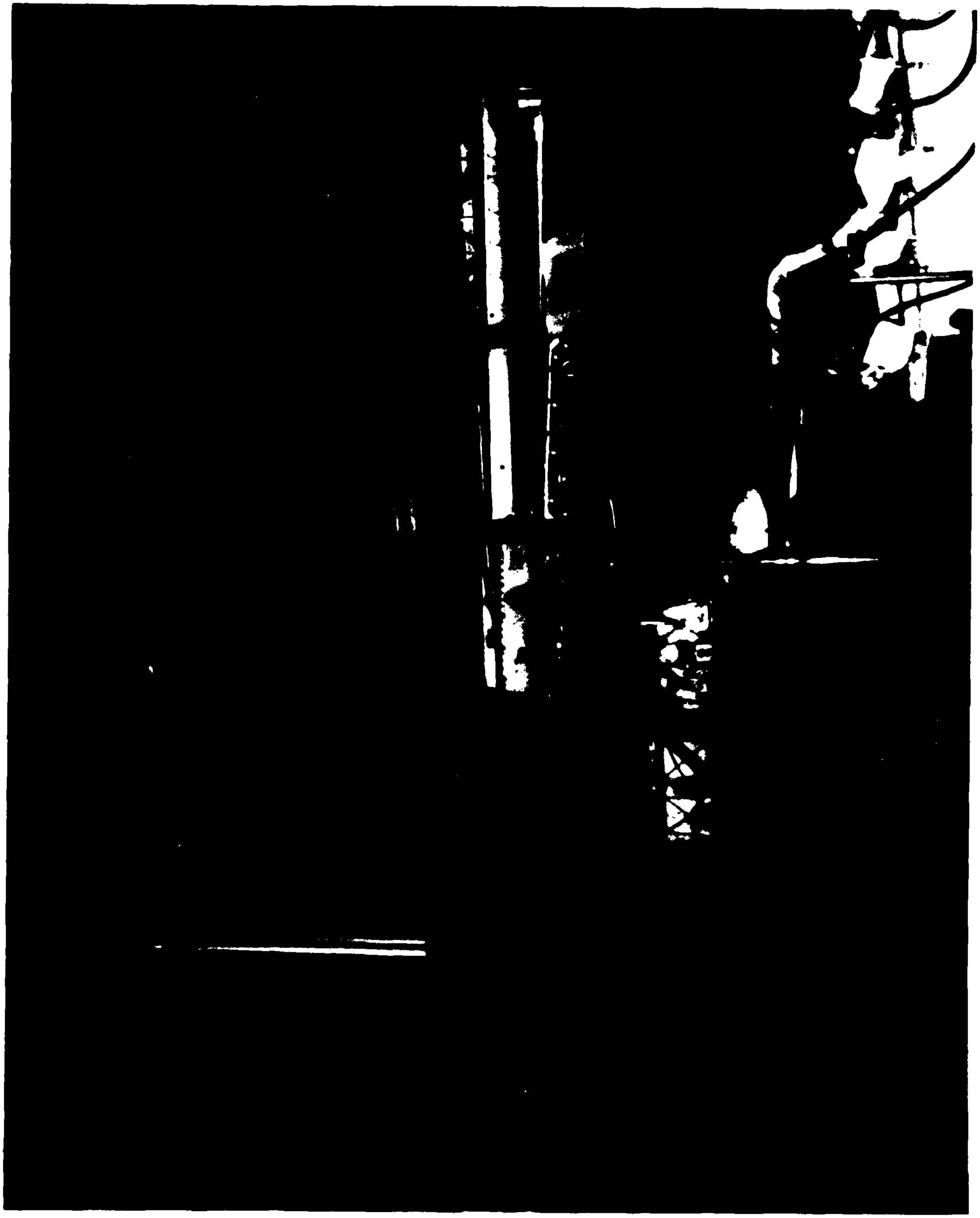
a. EPU Aircraft Maintenance: All aircraft maintenance was performed in a hanger at the General Dynamics, Fort Worth plant by General Dynamics employees using appropriate Aerospace Equipment Instructions (AEIs). During nitrogen depressurization and catalyst purge, technicians were wearing a face mask, apron, and gloves. During poppet valve replacement, no protective equipment was used.

(1) Nitrogen Depressurization (Photograph 1): Following hot firing of the EPU and before maintenance can be performed on the hydrazine cylinder, nitrogen pressure on the gas side of the cylinder must be relieved. This is accomplished by connecting a hose from the nitrogen vent valve on the cylinder and submersing the other end in a bucket of water placed on the ground. The nitrogen vent valve is slowly opened allowing depressurization of approximately 450 psi of nitrogen through the bubbling water. This task is accomplished by two technicians. For purposes of identification, the technician operating the vent valve is referred to as AC 1 and the technician holding the line in the bucket is referred to as AC 2.

(2) Catalyst Purge (Photographs 2 and 3): Removal of the hydrazine cylinder can be accomplished after disconnecting the hydrazine fuel line at the quick disconnect on the hydrazine end of the cylinder. The fuel line which leads to the catalyst bed and contains residual hydrazine is then connected to a portable ground nitrogen bottle. Pressure from this bottle is used to force the remaining hydrazine through the catalyst bed. Purging then continues with nitrogen for approximately one minute. In this study, technician AC 1 disconnected the hydrazine line from the fuel cylinder and reconnected it to the nitrogen purge bottle. This was accomplished while the technician was on the fuselage. Technician AC 2 positioned the nitrogen system on the ground near the leading edge of the starboard wing and operated the EPU controls in the cockpit during catalyst purging.

(3) Poppet Valve Replacement: The decomposition chamber (gas generator) poppet valve requires replacement each time the unit has been fired in the hydrazine mode. This task involves removal of the thermal insulation blanket surrounding the catalyst bed, removal of the poppet valve and replacement of the poppet valve shear pin. Technician AC 1 accomplished these actions during the study.

b. Hydrazine Cylinder Refilling: This task was conducted in the refilling facility at the General Dynamics, Fort Worth plant by General Dynamics personnel using appropriate AEIs. The bay doors on each end of the facility which normally allow natural ventilation during this procedure were closed for the study. This was done to facilitate evaluation



of personal exposure data during various stages of refilling. Since this action effectively eliminated the normal air change rate, all persons in the refilling facility were equipped with a full face demand type airline respirator. This equipment was in addition to the rubber gloves and apron normally required for servicing. The full face respirator was substituted for the normally required face shield. The doors were opened following each trial to permit the escape of any hydrazine vapor in the room.

(1) The procedures for refilling the partially used hydrazine cylinder involve the use of a specially designed fill stand (Photograph 4). The cylinder is placed in a sling above the fill table and then connected to a nitrogen cylinder and hydrazine drum. A technician connects all lines from the fill stand to the hydrazine cylinder and is responsible for replacing the burst disc once the cylinder is defueled. Cylinder connections are performed by a single technician referred to as RF 1. The second technician is responsible for calling out required tasks from the AEI and operating the valve controls (Photograph 5) on the fill stand. This technician is referred to as RF 2.

(2) When a cylinder is received at the refilling station, it is weighed on the sling. The partially filled cylinder is emptied by pressurizing the nitrogen side of the cylinder. Fuel flows into the hydrazine drum and pressure from the drum is vented through a partially filled water bucket located under the fill stand (Photograph 6). The burst disc is replaced after the cylinder is emptied (Photograph 7). The cylinder is filled from a hydrazine drum by applying nitrogen pressure to the headspace of the drum. Pressure on the nitrogen side of the filling cylinder is vented through the partially filled water bucket. The cylinder is determined to be filled when the total cylinder weight equals the empty weight as stamped on the cylinder plus 56 pounds. When the cylinder is filled, pressure from the hydrazine drum and residual hydrazine from the fill lines is purged through the bucket.

4. Results and Discussion

a. Breathing zone samples were collected for each worker performing tasks as presented in the Task Description. Notations introduced in that section are again used. Results which are reported for workers performing refill operations represent levels of exposure which employees would have received had they not been wearing air line respiratory protection.

b. Replicate samples were collected over the entire period for each maintenance activity and for short periods during which peak exposures were anticipated. These data are presented in Table 1 as parts per million of hydrazine in air adjusted to the ACGIH standard conditions of temperature and pressure. Figure 2 depicts the TWA breathing zone results for each task plus and minus one standard deviation. The TWA full period method of sampling provides an average exposure measurement which includes periods of no exposure, as well as periods of peak exposure. It cannot be used to assess peak exposure concentrations or their duration. For this reason and in an attempt to identify sources of hydrazine entering the work environment, additional short term samples were collected during each task in areas where peak concentrations of hydrazine were anticipated. These results are presented in Figure 3. The short bars at the bottom of Figure 3 are the TWA exposure ranges from Figure 2 for each of the tasks. They are included to show the relative differences in potential peak exposures versus TWA exposures.

c. The magnitude of the leak sources present in the refilling operations helps to explain the apparent variability seen in the TWA results for technician RF 1. Since the potential peak exposures are generally below the hydrazine odor threshold of 3 to 5 ppm, it would be possible for the technician to unknowingly place himself in exposure situations which are more than an order of magnitude above the TLV and the permissible excursion level of 0.3 ppm.

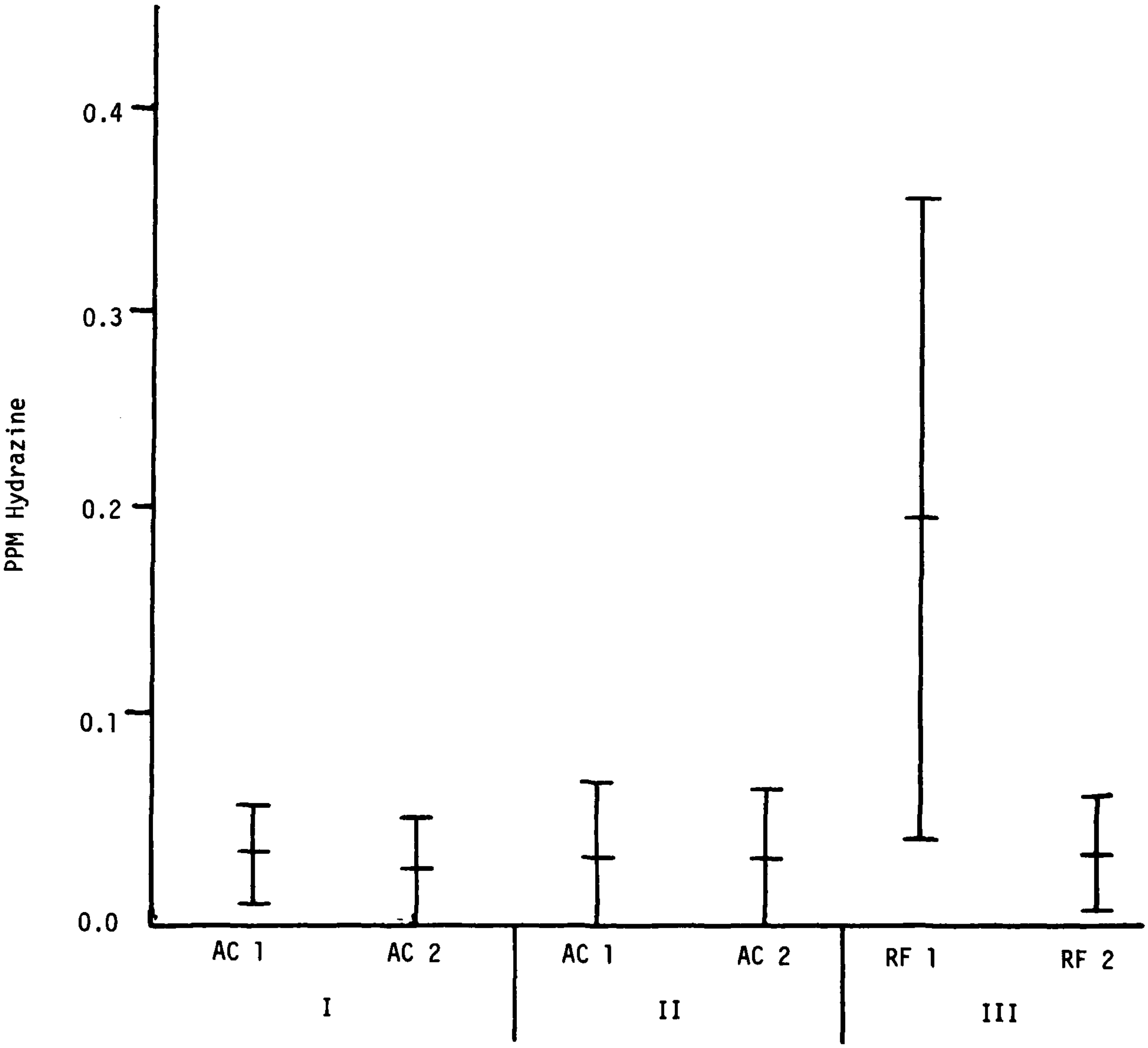
TABLE I

PERSONAL EXPOSURE TO HYDRAZINE, BY TASK

Task	Replications	Mean Conc (PPM)	Std Deviations
Nitrogen Depressurization and Catalyst Purge			
AC 1	6	0.03	0.02
AC 2	6	0.02	0.02
Poppet Valve Replacement			
AC 1	6	0.03	0.04
AC 2	6	0.03	0.03
Refill Stand (full period samples)			
RF 1	11	0.19	0.15
RF 2	10	0.03	0.02
Refill Stand (excursion samples)			
RF 1	3	0.14	0.15
RF 2	4	0.04	0.03

Note: Technician responsibilities are defined in Section 3.

HYDRAZINE EXPOSURE BY SPECIFIC TASK (Mean ± 1 Std Dev)

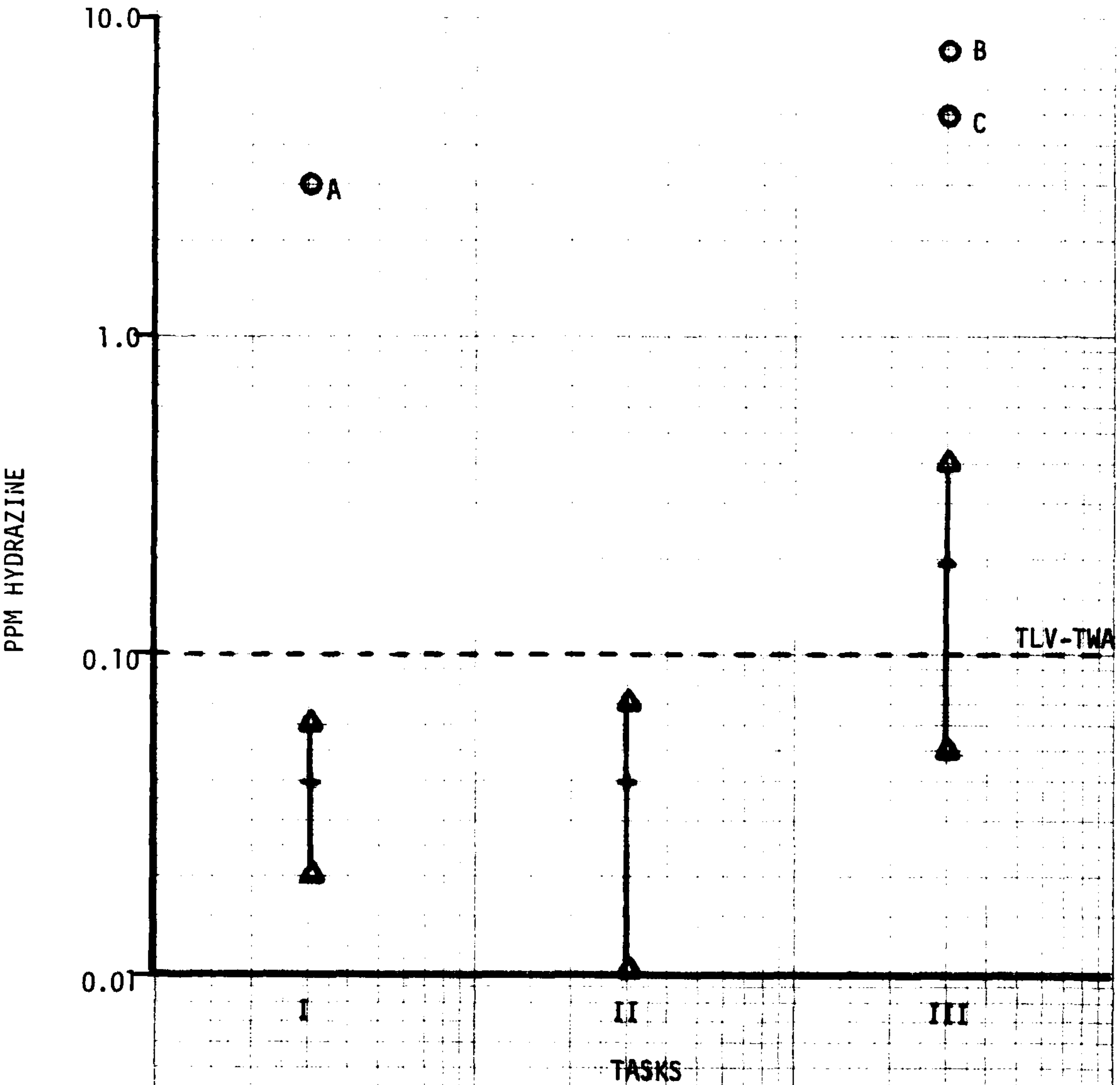


<u>TASK</u>

I - N_2 Depressurization and Catalyst Purge (requires approximately 60 min)
II - Poppet Valve Replacement (requires approximately 20 min)
III - Refilling (time varied from 1 to 3 hours)

FIGURE 2

POTENTIAL PEAK EXPOSURES IN RELATION TO TWA



A. Air above water bucket during N_2 Depressurization
B. Air above water bucket during Refill Operation
C. Air above hydrazine drum at Refill Operation

FIGURE 3

5. Recommendations

a. Engineering Modification

(1) Liquid scrubbing as used during nitrogen depressurization and refilling operations must be improved. Samples collected above the scrubbing bucket indicate that the efficiency of scrubbing is too low to guarantee an acceptable work environment for nearby technicians. Detachment 1, Armament Development and Test Center (ADTC) has been tasked by the SPO to develop an improved scrubbing device and/or an alternative collecting or neutralization media. The results of their study should be incorporated in the design of this procedure to eliminate potential exposure.

(2) During one of the catalyst purging operations, liquid hydrazine leaked from the line connection between the nitrogen servicing bottle and the hydrazine fuel line leading to the gas generator. This leak was easily corrected by tightening the connection, but it revealed a previously unknown contamination problem. Since the servicing bottle is on the ground and several feet below the gas generator, residual hydrazine flows from the gas generator fuel line to the nitrogen regulator once the connection is completed. There are several possible methods for correcting this problem. For example, a one-way valve could be incorporated in the connector. A more serious problem may involve the continued use of presently contaminated nitrogen servicing bottles since these systems are used for other purposes such as pressurizing struts and avionics equipment. The possibility of using hydrazine contaminated nitrogen in these systems and subsequent increased corrosion potential must be evaluated. A dedicated piece of support equipment for the nitrogen pressure supply should be considered.

(3) Plumbing and procedures on the fill stand should be re-evaluated to eliminate the need for purging liquid fuel into the scrubber.

(a) When the piston is forced to the hydrazine end of the cylinder during the draining portion of refilling, hydrazine flows from the cylinder back to the servicing drum. Residual hydrazine in the lines is then purged to the scrubber bucket. By placing a flask in line with the drain hose, a volume of 125 milliliters of liquid hydrazine was measured to be drained during this procedure (Photograph 8).

(b) Once the cylinder is filled, liquid fuel which remains in the filling lines is again purged to the scrubber instead of back to the fuel drum. Both this problem and the one identified in the previous paragraph can be corrected simultaneously. Refer to Figure 4 which is a duplicate of the schematic for the fill stand shown in General Dynamics AEI: 16 AEI-45-2001, 17 January 1977. At present, the valve leading

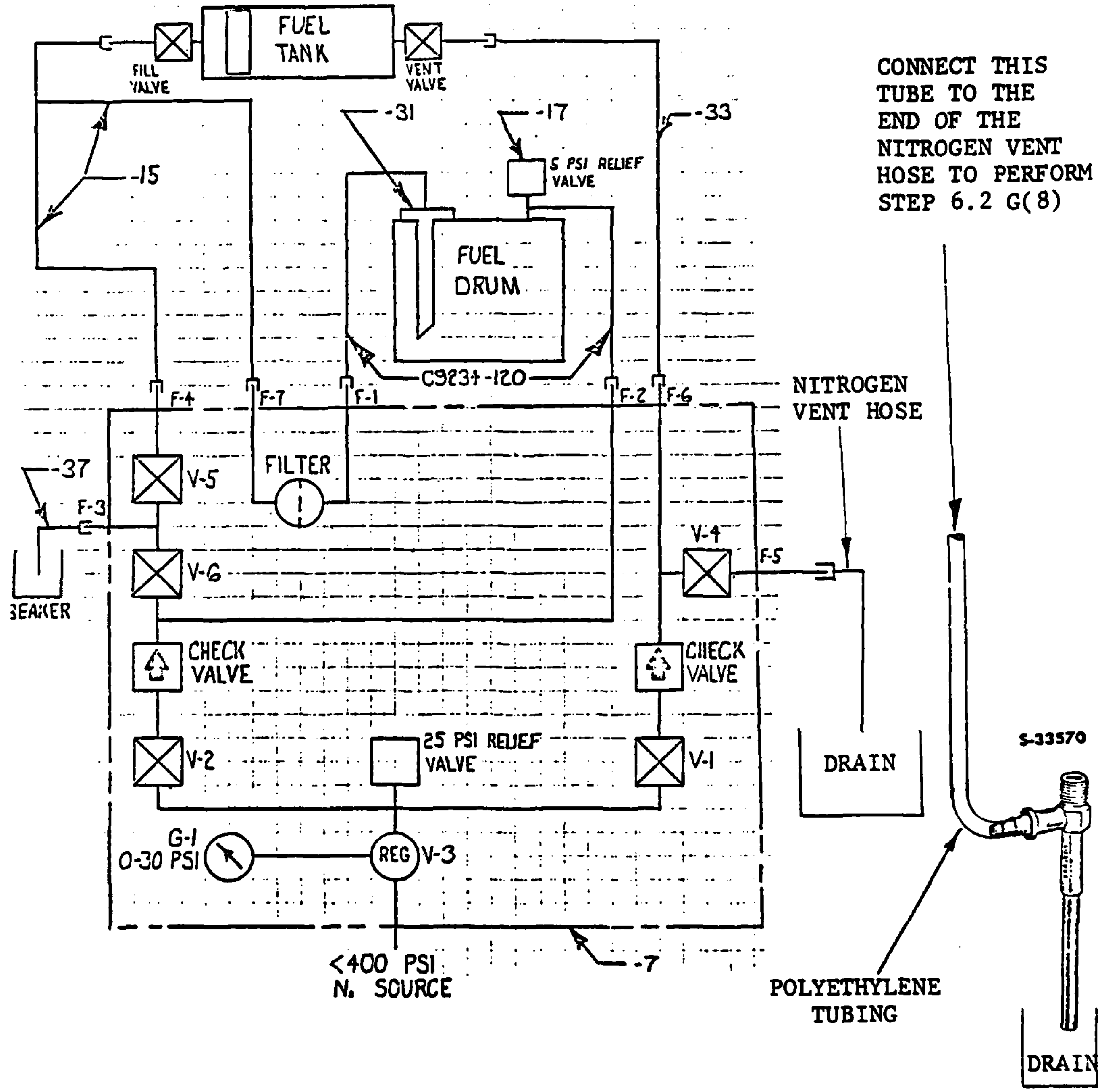


FIGURE 4. FUEL SERVICING SCHEMATIC

from F-3 connects with that leading from F-5 at a sight glass as shown in Photograph 4. An in-line trap positioned between F-3 and the sight glass which would later be drained to the fuel drum could be used to eliminate discharge of liquid fuel to the scrubber. We are confident that a number of other ways could be found to accomplish this same objective.

(4) During pressurization of the hydrazine drum for refilling the cylinder, samples collected around drum connections indicated excessive leaking of hydrazine vapor from pipe fittings into the workroom. A simple leak detection method should be developed and incorporated in refilling procedures to examine pipe connections with the intent of eliminating this unnecessary source of exposure. Commercially available direct reading detector tubes such as those manufactured by Mine Safety Appliance Company or Draeger Company are ideal for this purpose.

b. Protective Equipment

(1) Protective equipment is recommended for specific tasks with the intent of precluding exposures. These recommendations are based on the conditions observed during the survey and should be viewed as interim precautions pending elimination of hydrazine sources via engineering modification. Specific personal protective items are listed in Appendix A.

(a) Nitrogen Depressurization: For technicians AC 1 and AC 2:

(i) Clean long sleeve coveralls.

(ii) Full length rubber apron.

(iii) Forearm length rubber gloves.

(iv) A type "C" supplied air respirator as defined in AFOSH Standard 161-1. This selection has been based on the poor warning properties exhibited by hydrazine and the demonstrated presence of hydrazine at levels eighty times higher than the TLV-TWA.

(b) Catalyst Purge: Same equipment as described for nitrogen depressurization tasks.

(c) Poppet Valve Replacement: Coveralls and rubber gloves should be used by technician AC 1 since residual hydrazine may be present in the fuel lines following purging. It has been assumed that technician AC 2 is not directly involved in this task and that all small spills of liquid fuel have been removed from the EPU compartment prior to this task.

(d) Refilling Operations: Definition of respiratory protection for use during refilling in the final USAF facility will necessarily be dependent on the ventilation provided in the final design of the facility and an evaluation of personal exposure in that setting. Given the uncertainty of that final design at this time and the further uncertainty associated with pending regulatory efforts affecting permissible exposure to hydrazine, it is recommended that the final refill facility be designed to ventilate the actual refilling room as an isolated area from the rest of the facility. The room should also be equipped to provide compressed breathing air for type "C" supplied air respirators to be used by refilling maintenance teams. Other forms of respiratory protection should not be considered satisfactory. Additional personal protective equipment should include:

(i) Clean long sleeve coveralls.

(ii) Full length rubber apron.

(iii) Forearm length rubber gloves.

(iv) Rubber boots.

(2) Protective coveralls should be provided to each technician involved in the tasks described above. This clothing should be considered contaminated following use and should not be removed from the work area. Recommended procedures for the laundering of contaminated clothing are being developed by Det 1, ADTC.

c. Work Practices

(1) No smoking or eating should be permitted in any area where hydrazine systems are being serviced.

(2) Materials used to adsorb spills and any article of clothing which becomes contaminated with the fuel should be placed in a decontamination solution prior to laundering or final disposal. (As an interim recommendation, Det 1, ADTC suggests the use of a 5 percent chlorine bleach solution).

(3) Protective equipment must be routinely inspected and properly maintained.

(a) The degree of protection provided by specific pieces of protective equipment is dependent on the care which the equipment receives. Particularly for rubber items such as gloves, routine examination to inspect for cracks in the rubber is essential. The same is true for other items of equipment but gloves are emphasized since the potential for liquid contact is greatest there.

(b) Articles of protective equipment which have become contaminated with fuel should be decontaminated prior to removal. This should be accomplished by rinsing or wiping the items with a decontamination solution such as described earlier in this section. Care should be taken not to contaminate the wrong side of certain items of protective clothing such as gloves or aprons. Any items which become contaminated and cannot be cleaned should be eliminated from future use and replaced.

APPENDIX A

Personal Protective Equipment

The following items of personal protective equipment have been identified as being available through the federal supply system (NSN) except as noted.

1. Coveralls, Rocket Fuel Handlers

Resin modified, butyl coated acid and fuel resistant cotton airplane cloth. Designed for full protection. Ring insert and rolled wristlet sleeve closure, slide fastener, front closure garment fly with snap fasteners (MIL-C-43063).

8415-00-725-3627	Small
8415-00-725-3628	Medium
8415-00-725-3629	Large
8415-00-725-3630	X-Large
8415-00-725-3631	XX-Large

2. Alternative Coverall and Apron Skin Protection

a. Coveralls, antistatic polyester

8415-00-939-7879	Small
8415-00-939-7880	Medium
8415-00-939-7881	Large
8415-00-939-7882	X-Large

b. Apron, toxicological agent protective, mercerized cotton airplane cloth, butyl rubber coated both sides, olive drab, back closing tape, tape type fasteners at shoulders and back of waist, full length sleeves.

8415-00-281-7812	X-Small
8415-00-281-7813	Small
8415-00-281-7814	Medium
8415-00-281-7815	Long
8415-00-281-7816	X-Long

3. Boots, Rocket Fuel Handler

Black or maroon, butyl rubber coated upper, rubber bumper toe cap with steel toe reinforcement. Non-slip sole and heal, cloth cotton coated insole, ring type fastener, 10-1/2 inch high.

	Size
8430-00-782-3043	6
8430-00-782-3044	7
8430-00-782-3045	8
8430-00-782-3046	9

	Size
8430-00-782-3047	10
8430-00-782-3048	11
8430-00-782-3049	12
8430-00-782-3050	13

4. Faceshield

K11, plastic visor with forehead and semiskull guard, clear replaceable visor, tiltable visor included, head gear support, length 8 to 10 inches, width 17 to 19 inches, 0.040 inches thick.

4240-00-542-2048

5. Gloves, Rocket Fuel Handlers

Mens, lightweight butyl rubber impregnated with polyvinyl chloride rubber, collar cuff with closure ring. 12.125 inch length.

8415-00-952-3390	Small
8415-00-952-3391	Medium
8415-00-952-3392	Large

6. Respiratory Protection

a. Respiratory protection may be provided by any type-C supplied air respirator as listed in AFOSH Standard 161-1, Table II, part IV.

b. Compressed breathing air for flight line maintenance can be provided through the use of a compressor such as 4310-00-289-8249 and an air purifier assembly, 4310-00-173-0995.

APPENDIX B

Hydrazine Sampling and Analytical Methodology

1. The method used for sampling hydrazine in air involved collection of hydrazine on a solid media with subsequent acid extraction and analysis using a Hach colorimeter. The specific method was developed and validated by the Crew Environments Branch of the USAF School of Aerospace Medicine, Brooks AFB TX.

2. Breathing zone samples were collected using 6 millimeter inside diameter glass tubing which had been packed with a total of 300 milligrams of 60-80 mesh Chromosorb RA coated with 20 percent concentrated sulfuric acid. The pressure drop while using these tubes at a flow rate of 1.5 liters per minute remained relatively stable, ranging from 12 to 14 inches of water. Earlier attempts involved the use of the Los Alamos Scientific Laboratory technique employing silica gel as a support media. This method was abandoned after testing indicated a variable pressure drop as a function of sampling time. This variation has been attributed to the influence of relative humidity on the consistency of the support media.

3. The sampling methodology has been validated for hydrazine concentrations from 0.05 to 100 ppm using 40 and 70 percent relative humidity air at temperatures varying from 0° to 25°C. Flow rates were varied from 0.2 to 1.5 liters per minute. Hydrazine stability on the sorbent was verified by passing pure air through loaded tubes for up to eight hours with subsequent storage for two weeks prior to analysis. No statistically significant loss in hydrazine was noted. Verification of the hydrazine concentrations delivered to each tube was conducted by intermittent analysis using standard impinger and wet chemistry methods and using a prototype chemiluminescent hydrazine analyzer.

4. Analysis used desorption of hydrazine with 0.1 normal sulfuric acid followed by addition of p-dimethylaminobenzaldehyde (PDAB) to form a yellow-orange color complex. The intensity of this complex was interpreted by measuring the absorbance of light at a wavelength of 458 nanometers using a Hach spectrophotometer. Methylhydrazine would also be measured using this technique but since there is none in the H-70, this was not a concern.

5. The analytical technique has a sensitivity of 1 microgram. The USAFSAM validation studies indicate that the collection and desorption are virtually 100 percent efficient.

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F-16 Update, June 1978

Several actions have been taken by both the contractor and F-16 Systems Program Office since this study was conducted in Jaunary 1978. These changes are directed toward reducing maintenance crew exposures to hydrazine while working on or around the F-16 emergency power unit.

1. The bucket of water which was used during nitrogen depressurization of the on-board system is being replaced with a more efficient scrubbing system. The first of those systems is in production now and depending on the results of scrubbing efficiency tests; it will use either water or a neutralizer such as used during spill clean-ups (household bleach).

2. The refilling stand has been reengineered to provide a separate tank for holding waste fuel. A scrubbing device has been designed and will be installed beneath the refilling table. General Dynamics engineers are evaluating a proposal to "top off" the EPU tanks instead of first emptying them prior to refilling. A decision on that proposal has not been made as of June 1978.

3. Studies conducted by the School of Aerospace Medicine have shown that small quantities of unreacted hydrazine may be present in the EPU exhaust gas in addition to large quantities of ammonia. A method to prevent the system from inadvertently firing on the ground has been incorporated on the production aircraft. In addition, the need for ground firing the system at periodic intervals is being eliminated.

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